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(71) Applicant : **ETHYL PETROLEUM ADDITIVES,
INC.
20 South Fourth Street
St. Louis Missouri 63102-1886 (US)**

(72) Inventor : **Henderson, Douglas Harold
Route 3, Box 786
Glen Allen, Virginia 23060 (US)**

(74) Representative : **Collier, Jeremy Austin Grey
J.A. Kemp & Co., 14 South Square, Gray's Inn
London WC1R 5LX (GB)**

(54) **Unleaded aviation gasoline.**

(57) An unleaded aviation gasoline composition which comprises a blend of hydrocarbons and at least one cyclopentadienyl manganese tricarbonyl compound dissolved therein in an amount such that the composition has a minimum knock value lean rating octane number of 100 as determined by ASTM Test Method D2700 and wherein Motor Method octane ratings are converted to aviation ratings in the manner described in ASTM Specification D910-90, the composition being further characterized by having : a) a distillation temperature by ASTM Test Method D86 of 10% evaporated, 167°F maximum temperature ; 40% evaporated, 167°F maximum temperature ; 90% evaporated, 275°F maximum temperature ; and a final boiling point of 338°F maximum temperature ; the sum of the 10 and 50% evaporated temperatures being 307°F minimum ; the distillation recovery being 97% minimum ; the distillation residue being 1.5% maximum ; and the distillation loss being 1.5% maximum ; b) a heat of combustion by ASTM Test Method D1405 and as calculated from Table 1 thereof of 18,720 btu per pound minimum, or a heat of combustion by ASTM Test Method D2382 of 18,700 btu per pound minimum, the latter method controlling in case of a discrepancy therebetween ; c) a vapor pressure by ASTM Test Method D323 or D2551 of 5.5 psi minimum and 7.0 psi maximum ; d) a copper strip corrosion by ASTM Test Method D130 of number 1, maximum ; e) a potential gum (5-hour aging gum) by ASTM Test Method D873 of 6 mg per 100 mL maximum, or a potential gum (16-hour aging gum by ASTM Test Method D873) of 10 mg per 100 mL ; f) a sulfur content by ASTM Test Method D1266 or D2622 of 0.05% by weight maximum ; g) a freezing point by ASTM Test Method D2386 of -72°F maximum ; and h) a water reaction by ASTM Test Method D1094 wherein the volume change, if any, does not exceed ± 2 mL.

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This invention relates to unleaded aviation gasoline compositions which satisfy the specification requirements of ASTM Specification D910-90.

The specifications imposed upon aviation gasolines are necessarily extremely rigorous, since the consequences could be disastrous if an aviation gasoline does not perform properly in a spark-ignition aviation engine.

While leaded aviation gasolines have performed wonderfully well in actual service for many years, many misguided persons have clamored for elimination of lead from gasoline. If their efforts succeed, the refining industry will be faced with the problem of trying to provide unleaded aviation gasoline that performs as well as leaded aviation gasoline and that does not exceed the economic constraints of the marketplace.

10 This invention is deemed to overcome the above problem most expeditiously.

In accordance with this invention, there is provided an unleaded aviation gasoline composition which comprises a blend of hydrocarbons and at least one cyclopentadienyl manganese tricarbonyl compound dissolved therein in an amount such that said gasoline composition has a minimum knock value lean rating octane number of 100 as determined by ASTM Test Method D2700 and wherein Motor Method octane ratings are converted to aviation ratings in the manner described in ASTM Specification D910-90, said composition being further characterized by having: a) a distillation temperature as determined by ASTM Test Method D86 of 10% evaporated, 167°F maximum temperature; 40% evaporated, 167°F maximum temperature; 90% evaporated, 275°F maximum temperature; and a final boiling point of 338°F maximum temperature; the sum of the 10 and 50% evaporated temperatures being 307°F minimum; the distillation recovery being 97% minimum; the distillation residue being 1.5% maximum; and the distillation loss being 1.5% maximum; b) a heat of combustion as determined by ASTM Test Method D1405 and as calculated from Table 1 thereof of 18,720 btu per pound minimum, or a heat of combustion as determined by ASTM Test Method D2382 of 18,700 btu per pound minimum, the latter method controlling in case of a discrepancy therebetween; c) a vapor pressure as determined by ASTM Test Method D323 or D2551 of 5.5 psi minimum and 7.0 psi maximum; d) a copper strip corrosion as determined by ASTM Test Method D130 of number 1, maximum; e) a potential gum (5-hour aging gum) as determined by ASTM Test Method D873 of 6 mg per 100 mL maximum, or a potential gum (16-hour aging gum as determined by ASTM Test Method D873) of 10 mg per 100 mL; f) a sulfur content as determined by ASTM Test Method D1266 or D2622 of 0.05% by weight maximum; g) a freezing point as determined by ASTM Test Method D2386 of -72°F maximum; and h) a water reaction as determined by ASTM Test Method D1094 wherein the volume change, if any, does not exceed ± 2 mL.

Preferred gasoline compositions are those in which the gasoline composition additionally has a minimum performance number reported to the nearest whole number and as determined by ASTM Test Method D909 of 130. In this connection, a minimum performance number of 130 is equivalent to a knock value determined using isoctane plus 1.28 milliliters of tetraethyllead per gallon.

35 Another embodiment of this invention provides the method of operating a four stroke cycle, reciprocating piston aircraft engine which comprises providing or using as the fuel for said engine a gasoline composition of this invention.

Still another embodiment of this invention provides, in combination, at least one four stroke cycle, reciprocating piston aircraft engine and at least one fuel storage tank operatively connected with said at least one engine so as to deliver fuel required to operate said engine, said at least one fuel storage tank containing a gasoline composition of this invention as the fuel for said engine.

Cyclopentadienyl manganese tricarbonyl compounds which can be used in the practice of this invention include cyclopentadienyl manganese tricarbonyl, methylcyclopentadienyl manganese tricarbonyl, dimethylcyclopentadienyl manganese tricarbonyl, trimethylcyclopentadienyl manganese tricarbonyl, tetramethylcyclopentadienyl manganese tricarbonyl, pentamethylcyclopentadienyl manganese tricarbonyl, ethylcyclopentadienyl manganese tricarbonyl, diethylcyclopentadienyl manganese tricarbonyl, propylcyclopentadienyl manganese tricarbonyl, isopropylcyclopentadienyl manganese tricarbonyl, tert-butylcyclopentadienyl manganese tricarbonyl, octylcyclopentadienyl manganese tricarbonyl, dodecylcyclopentadienyl manganese tricarbonyl, ethylmethylcyclopentadienyl manganese tricarbonyl, and indenyl manganese tricarbonyl, including mixtures of two or more such compounds. Preferred are the cyclopentadienyl manganese tricarbonyls which are liquid at room temperature such as methylcyclopentadienyl manganese tricarbonyl, ethylcyclopentadienyl manganese tricarbonyl, liquid mixtures of cyclopentadienyl manganese tricarbonyl and methylcyclopentadienyl manganese tricarbonyl, and mixtures of methylcyclopentadienyl manganese tricarbonyl and ethylcyclopentadienyl manganese tricarbonyl. Preparation of such compounds is described in the literature, for example, U.S. 50 2,818,417.

In another preferred embodiment the unleaded gasoline composition additionally contains at least one antioxidant in an amount not in excess of 8.4 pounds per 1000 barrels, said antioxidant being selected from the group N,N'-diisopropyl-p-phenylenediamine, N,N'-di-sec-butyl-p-phenylenediamine, 2,4-dimethyl-6-tert-butyl-

phenol, 2,6-di-tert-butyl-4-methylphenol, 2,6-di-tert-butylphenol, a mixture of 75% minimum 2,6-di-tert-butylphenol plus 25% maximum di- and tri-tert-butylphenol; and a mixture of 75% minimum di- and triisopropyl phenols plus 25% maximum di- and tri-tert-butylphenol. Most preferably the amount of such antioxidant does not exceed 4.2 pounds per 1000 barrels.

5 It is to be understood that the fuels of this invention are unleaded in the sense that a lead-containing antiknock agent is not deliberately added to the gasoline. Trace amounts of lead due to contamination of equipment or like circumstances are permissible and are not to be deemed excluded from the practice of this invention.

10 The base fuels used in the foregoing compositions can be blends of refined hydrocarbon derived from crude petroleum, natural gasoline, or blends thereof with synthetic hydrocarbons or aromatic hydrocarbons, or both. Blending components, if approved for use in aviation gasolines, such as oxygenated ingredients, can be included. Rarely, if ever, will the content of aromatic hydrocarbons in the gasoline exceed levels above 25%. As noted above, the overall composition must satisfy the requirements a) through h) inclusive as set forth above.

15 Other components which can be employed, and under certain circumstances are preferably employed, include dyes which do not contribute to excessive induction system deposits. Typical dyes which can be employed are 1,4-dialkylaminanthraquinone, p-diethylaminoazobenzene (Color Index No. 11020) or Color Index Solvent Yellow No. 107, methyl derivatives of azobenzene-4-azo-2-naphthol (methyl derivatives of Color Index No. 26105), alkyl derivatives of azobenzene-4-azo-2-naphthol, or equivalent materials. The amounts used should, wherever possible, conform to the limits specified in ASTM Specification D910-90.

20 Fuel system icing inhibitors may also be included in the fuels of this invention. Preferred are ethylene glycol monomethyl ether and isopropyl alcohol, although materials giving equivalent performance may be considered acceptable for use. Amounts used should, wherever possible, conform to the limits referred to in ASTM Specification D910-90.

25 The concentration of the cyclopentadienyl manganese tricarbonyl compound used in the unleaded aviation gasoline base stock satisfying the above criteria will vary to some extent depending upon the identity and properties of the base fuel and the octane quality desired in the finished fuel. Ordinarily amounts equivalent to 0.01-0.5 gram of manganese per gallon of fuel are sufficient, although higher amounts can be used whenever deemed necessary or appropriate, provided that the resultant fuel composition satisfies the requirements of a) through h) above. Preferably the fuel will contain up to 0.25 gram of manganese per gallon as one or more cyclopentadienyl manganese tricarbonyl compounds.

30 There are good and sufficient reasons why the gasoline composition is to comply with the requirements set forth above as a) through h). The rationale behind these requirements as set forth in ASTM Specification D910-90 are as follows:

35 "X1.1.1. Aviation gasoline is a complex mixture of relatively volatile hydrocarbons that vary widely in their physical and chemical properties. The engines and aircraft impose a variety of mechanical, physical, and chemical environments. The properties of aviation gasoline ... must be properly balanced to give satisfactory engine performance over an extremely wide range of conditions.

40 X1.1.3. Specifications covering antiknock quality define the grades of aviation gasoline. The other requirements either prescribe the proper balance of properties to ensure satisfactory engine performance or limit components of undesirable nature to concentrations so low that they will not have an adverse effect on engine performance.

45 X1.2.1. The fuel-air mixture in the cylinder of a spark-ignition engine will, under certain conditions, ignite spontaneously in localized areas instead of progressing from the spark. This may cause a detonation or knock, usually inaudible in aircraft engines. This knock, if permitted to continue for more than brief periods, may result in serious loss of power and damage to or destruction of the aircraft engine. When aviation gasoline is used in other types of aviation engines, for example, in certain turbine engines where specifically permitted by the engine manufacturers, knock or detonation characteristics may not be critical requirements." In accordance with other preferred embodiments this invention further provides:

50 A) The method of operating a four stroke cycle, reciprocating piston aircraft engine which comprises providing and/or using as the fuel for said engine a gasoline composition of this invention, and providing and/or using as the lubricating oil for said engine a lubricating oil composition satisfying the chemical and physical property requirements set forth below; and

55 B) Apparatus which comprises in combination (i) at least one four stroke cycle, reciprocating piston aircraft engine, (ii) at least one fuel storage tank operatively connected with said at least one engine so as to deliver fuel required to operate said engine, and (iii) at least one chamber in said engine for receiving and maintaining a supply of lubricating oil for lubricating said engine during operation thereof, said at least one fuel storage tank containing a gasoline composition of this invention as the fuel for said engine and said at

least one chamber containing as the lubricating oil for said engine a lubricating oil composition satisfying the chemical and physical property requirements set forth below.

The chemical and physical property requirements of the lubricating oil used in the foregoing preferred embodiments A) and B) are as follows:

- 5 1) Viscosity, cSt, per ASTM D 445:

| | <u>SAE Grade</u> | <u>Minimum at 100°C</u> | <u>Less than at 100°C</u> |
|----|------------------|-------------------------|---------------------------|
| 10 | 30 | 9.3 | 12.5 |
| | 40 | 12.5 | 16.3 |
| | 50 | 16.3 | 21.9 |
| | 60 | 21.9 | 26.1 |

- 15 2) Multigrade oil shall meet the viscosity requirements and the Low Temperature Viscosity Cold Crank Simulation requirements of SAE Test Method J300 for the designated grade.
- 3) Viscosity Index, minimum per ASTM D 2270: 100 for SAE grades 30, 40 and Multigrade; 95 for SAE grades 50 and 60.
- 20 4) Flash Point, °C, minimum per ASTM D 92: 220 for SAE grades 30 and Multigrade; 225 for SAE grade 40; and 243 for SAE grades 50 and 60.
- 5) Pour Point, °C, maximum per ASTM D 97: -24 for SAE grade 30; -22 for SAE grade 40; and -18 for SAE grades 50 and 60.
- 25 6) Viscosity, High Temperature, High Shear at 150°C, cP, minimum per ASTM D 4683, D 4741, D 4624: 3.3 for all viscosity grades.
- 7) Total Acid Number, mg KOH/g, maximum (titrated to a pH 11 end point) per ASTM D 664: 1.0 for all viscosity grades.
- 25 8) Ash Content, Mass %, maximum per ASTM D 482: 0.006 for all viscosity grades.
- 9) Trace Sediment, mL/100 mL Oil, maximum per ASTM D 2273: 0.005 for all viscosity grades.
- 30 10) Copper Strip Corrosion, maximum rating per ASTM D 130: 1 after 3 hours @ 100 °C for all viscosity grades; and 3 after 3 hours @ 204 °C for all viscosity grades.
- 11) Foaming Tendency/Stability per ASTM D 892: Aerated Volume, mL, maximum for all viscosity grades per Sequences I, II and III: 50; Volume after 10 minutes, mL, maximum for all viscosity grades per Sequences I, II, and III: 0.
- 35 12) Compatibility with other oils per FTM 791 Method 3403: All viscosity grades shall pass.
- 13) Elastomer Compatibility, % swelling, acceptable range for all viscosity grades after 72 hours per FTM 791 Method 3604 (except conducted with the specific materials and temperatures herein listed):

| | <u>Material</u> | <u>Test Temperature</u> | <u>Acceptable Limits</u> |
|----|-------------------------|-------------------------|--------------------------|
| 40 | AMS-3217/1 | 70°C (158°F) | - 5 to + 5 |
| | AMS-3217/4 | 150°C (302°F) | - 5 to + 5 |
| | AMS-3217/5 | 150°C (302°F) | - 5 to + 5 |
| | US Navy Silicone Rubber | 121°C (250°F) | 0 to + 20 |

- 45 14) Trace Metal Content, ppm, maximum for all viscosity grades, per test method of Paragraph 4.5.2 of MIL-L-22851D (1 December 1990) or equivalent: Iron, 5; Silver, 3; Aluminum, 7; Chromium, 5; Copper, 3; Magnesium, 3; Nickel, 3; Lead, 5; Silicon, 25; Tin, 10; Titanium, 2; Molybdenum, 4. The most preferred lubricating oils will not only meet the above requirements 1) through 14) but in addition, will meet the following L-38 Engine Test Requirements:
- 15) Total Bearing Weight Loss, mg, maximum per ASTM STP 509A, Part IV for all viscosity grades: 500.
- 16) Used Oil Viscosity, Stripped, maximum % Change @ 40°C per ASTM D 445 for all single viscosity grades: -15 to + 10.
- 50 17) Used Oil Viscosity at 100°C of Multi-grade Oil per SAE J300 shall remain in SAE J300 grade.
- 18) Used Oil Total Acid Number, maximum change for all viscosity grades per ASTM D 664 (titrated to a pH 11 end point): 2.0.

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Claims

1. An unleaded aviation gasoline composition which comprises a blend of hydrocarbons and at least one

5 cyclopentadienyl manganese tricarbonyl compound dissolved therein in an amount such that said gasoline composition has a minimum knock value lean rating octane number of 100 as determined by ASTM Test Method D2700 and wherein Motor Method octane ratings are converted to aviation ratings in the manner described in ASTM Specification D910-90, said composition being further characterized by having:

- 10 a) a distillation temperature as determined by ASTM Test Method D86 of 10% evaporated, 167°F maximum temperature; 40% evaporated, 167°F maximum temperature; 90% evaporated, 275°F maximum temperature; and a final boiling point of 338°F maximum temperature; the sum of the 10 and 50% evaporated temperatures being 307°F minimum; the distillation recovery being 97% minimum; the distillation residue being 1.5% maximum; and the distillation loss being 1.5% maximum;
 - 15 b) a heat of combustion as determined by ASTM Test Method D1405 and as calculated from Table 1 thereof of 18,720 btu per pound minimum, or a heat of combustion as determined by ASTM Test Method D2382 of 18,700 btu per pound minimum, the latter method controlling in case of a discrepancy therebetween;
 - 20 c) a vapor pressure as determined by ASTM Test Method D323 or D2551 of 5.5 psi minimum and 7.0 psi maximum;
 - d) a copper strip corrosion as determined by ASTM Test Method D130 of number 1, maximum;
 - e) a potential gum (5-hour aging gum) as determined by ASTM Test Method D873 of 6 mg per 100 mL maximum, or a potential gum (16-hour aging gum as determined by ASTM Test Method D873) of 10 mg per 100 mL;
 - f) a sulfur content as determined by ASTM Test Method D1266 or D2622 of 0.05 % by weight maximum;
 - 25 g) a freezing point as determined by ASTM Test Method D2386 of -72°F maximum; and
 - h) a water reaction as determined by ASTM Test Method D1094 wherein the volume change, if any, does not exceed ± 2 mL.
2. A composition as claimed in Claim 1 wherein said gasoline composition has a minimum knock value lean rating octane number of 100 as determined by ASTM Test Method D2700 and a minimum performance number reported to the nearest whole number and as determined by ASTM Test Method D909 of 130.
- 30 3. A composition as claimed in Claim 1 wherein said cyclopentadienyl manganese tricarbonyl compound consists essentially of methylcyclopentadienyl manganese tricarbonyl.
4. The method of operating a four stroke cycle, reciprocating piston aircraft engine which comprises providing or using as the fuel for said engine an unleaded aviation gasoline composition which comprises a blend of hydrocarbons and at least one cyclopentadienyl manganese tricarbonyl compound dissolved therein in an amount such that said gasoline composition has a minimum knock value lean rating octane number of 100 as determined by ASTM Test Method D2700 and wherein Motor Method octane ratings are converted to aviation ratings in the manner described in ASTM Specification D910-90, said composition being further characterized by having:
- 40 a) a distillation temperature as determined by ASTM Test Method D86 of 10% evaporated, 167°F maximum temperature; 40% evaporated, 167°F maximum temperature; 90% evaporated, 275°F maximum temperature; and a final boiling point of 338°F maximum temperature; the sum of the 10 and 50% evaporated temperatures being 307°F minimum; the distillation recovery being 97% minimum; the distillation residue being 1.5% maximum; and the distillation loss being 1.5% maximum;
 - 45 b) a heat of combustion as determined by ASTM Test Method D1405 and as calculated from Table 1 thereof of 18,720 btu per pound minimum, or a heat of combustion as determined by ASTM Test Method D2382 of 18,700 btu per pound minimum, the latter method controlling in case of a discrepancy therebetween;
 - c) a vapor pressure as determined by ASTM Test Method D323 or D2551 of 5.5 psi minimum and 7.0 psi maximum;
 - d) a copper strip corrosion as determined by ASTM Test Method D130 of number 1, maximum;
 - e) a potential gum (5-hour aging gum) as determined by ASTM Test Method D873 of 6 mg per 100 mL maximum, or a potential gum (16-hour aging gum as determined by ASTM Test Method D873) of 10 mg per 100 mL;
 - f) a sulfur content as determined by ASTM Test Method D1266 or D2622 of 0.05% by weight maximum;
 - 50 g) a freezing point as determined by ASTM Test Method D2386 of -72°F maximum; and
 - h) a water reaction as determined by ASTM Test Method D1094 wherein the volume change, if any, does not exceed ± 2 mL.

5. A method as claimed in Claim 4 wherein said gasoline composition has a minimum knock value lean rating octane number of 100 as determined by ASTM Test Method D2700 and a minimum performance number reported to the nearest whole number and as determined by ASTM Test Method D909 of 130.
- 5 6. A method as claimed in Claim 4 wherein said cyclopentadienyl manganese tricarbonyl compound consists essentially of methylcyclopentadienyl manganese tricarbonyl.
- 10 7. Apparatus which comprises, in combination, at least one four stroke cycle, reciprocating piston aircraft engine and at least one fuel storage tank operatively connected with said at least one engine so as to deliver fuel required to operate said engine, said at least one fuel storage tank containing as the fuel for said engine an unleaded aviation gasoline composition which comprises a blend of hydrocarbons and at least one cyclopentadienyl manganese tricarbonyl compound dissolved therein in an amount such that said gasoline composition has a minimum knock value lean rating octane number of 100 as determined by ASTM Test Method D2700 and wherein Motor Method octane ratings are converted to aviation ratings in the manner described in ASTM Specification D910-90, said composition being further characterized by having:
- 15 a) a distillation temperature as determined by ASTM Test Method D86 of 10% evaporated, 167°F maximum temperature; 40% evaporated, 167°F maximum temperature; 90% evaporated, 275°F maximum temperature; and a final boiling point of 338°F maximum temperature; the sum of the 10 and 50% evaporated temperatures being 307°F minimum; the distillation recovery being 97% minimum; the distillation residue being 1.5% maximum; and the distillation loss being 1.5% maximum;
- 20 b) a heat of combustion as determined by ASTM Test Method D1405 and as calculated from Table 1 thereof of 18,720 btu per pound minimum, or a heat of combustion as determined by ASTM Test Method D2382 of 18,700 btu per pound minimum, the latter method controlling in case of a discrepancy therebetween;
- 25 c) a vapor pressure as determined by ASTM Test Method D323 or D2551 of 5.5 psi minimum and 7.0 psi maximum;
- d) a copper strip corrosion as determined by ASTM Test Method D130 of number 1, maximum;
- 30 e) a potential gum (5-hour aging gum) as determined by ASTM Test Method D873 of 6 mg per 100 mL maximum, or a potential gum (16-hour aging gum as determined by ASTM Test Method D873) of 10 mg per 100 mL;
- f) a sulfur content as determined by ASTM Test Method D1266 or D2622 of 0.05 % by weight maximum;
- 35 g) a freezing point as determined by ASTM Test Method D2386 of -72°F maximum; and
- h) a water reaction as determined by ASTM Test Method D1094 wherein the volume change, if any, does not exceed ± 2 mL.
8. Apparatus as claimed in Claim 7 wherein said cyclopentadienyl manganese tricarbonyl compound consists essentially of methylcyclopentadienyl manganese tricarbonyl.
- 40 9. The method of operating a four stroke cycle, reciprocating piston aircraft engine which comprises:
A) providing and/or using as the fuel for said engine an unleaded aviation gasoline composition which comprises a blend of hydrocarbons and at least one cyclopentadienyl manganese tricarbonyl compound dissolved therein in an amount such that said gasoline composition has a minimum knock value lean rating octane number of 100 as determined by ASTM Test Method D2700 and wherein Motor Method octane ratings are converted to aviation ratings in the manner described in ASTM Specification D910-90, said composition being further characterized by having:
- 45 a) a distillation temperature as determined by ASTM Test Method D86 of 10% evaporated, 167°F maximum temperature; 40% evaporated, 167°F maximum temperature; 90% evaporated, 275°F maximum temperature; and a final boiling point of 338°F maximum temperature; the sum of the 10 and 50% evaporated temperatures being 307°F minimum; the distillation recovery being 97% minimum; the distillation residue being 1.5% maximum; and the distillation loss being 1.5% maximum;
- 50 b) a heat of combustion as determined by ASTM Test Method D1405 and as calculated from Table 1 thereof of 18,720 btu per pound minimum, or a heat of combustion as determined by ASTM Test Method D2382 of 18,700 btu per pound minimum, the latter method controlling in case of a discrepancy therebetween;
- c) a vapor pressure as determined by ASTM Test Method D323 or D2551 of 5.5 psi minimum and 7.0 psi maximum;
- 55 d) a copper strip corrosion as determined by ASTM Test Method D130 of number 1, maximum;

e) a potential gum (5-hour aging gum) as determined by ASTM Test Method D873 of 6 mg per 100 mL maximum, or a potential gum (16-hour aging gum as determined by ASTM Test Method D873) of 10 mg per 100 mL;

5 f) a sulfur content as determined by ASTM Test Method D1266 or D2622 of 0.05 % by weight maximum;

g) a freezing point as determined by ASTM Test Method D2386 of -72°F maximum; and

10 h) a water reaction as determined by ASTM Test Method D1094 wherein the volume change, if any, does not exceed ± 2 mL; and

B) providing and/or using as the lubricating oil for said engine a lubricating oil composition satisfying the following chemical and physical property requirements:

1) Viscosity, cSt, per ASTM D 445:

| <u>SAE Grade</u> | <u>Minimum at 100°C</u> | <u>Less than at 100°C</u> |
|------------------|-------------------------|---------------------------|
| 15 30 | 9.3 | 12.5 |
| 40 | 12.5 | 16.3 |
| 50 | 16.3 | 21.9 |
| 60 | 21.9 | 26.1 |

20 2) Multigrade oil shall meet the viscosity requirements and the Low Temperature Viscosity Cold Crank Simulation requirements of SAE Test Method J300 for the designated grade.

3) Viscosity Index, minimum per ASTM D 2270: 100 for SAE grades 30, 40 and Multigrade; 95 for SAE grades 50 and 60.

25 4) Flash Point, °C, minimum per ASTM D 92: 220 for SAE grades 30 and Multigrade; 225 for SAE grade 40; and 243 for SAE grades 50 and 60.

5) Pour Point, °C, maximum per ASTM D 97: -24 for SAE grade 30; -22 for SAE grade 40; and -18 for SAE grades 50 and 60.

6) Viscosity, High Temperature, High Shear at 150°C, cP, minimum per ASTM D 4683, D 4741, D 4624: 3.3 for all viscosity grades.

30 7) Total Acid Number, mg KOH/g, maximum (titrated to a pH 11 end point) per ASTM D 664: 1.0 for all viscosity grades.

8) Ash Content, Mass %, maximum per ASTM D 482: 0.006 for all viscosity grades.

9) Trace Sediment, mL/100 mL Oil, maximum per ASTM D 2273: 0.005 for all viscosity grades.

35 10) Copper Strip Corrosion, maximum rating per ASTM D 130: 1 after 3 hours @ 100°C for all viscosity grades; and 3 after 3 hours @ 204°C for all viscosity grades.

11) Foaming Tendency/Stability per ASTM D 892: Aerated Volume, mL, maximum for all viscosity grades per Sequences I, II and III: 50; Volume after 10 minutes, mL, maximum for all viscosity grades per Sequences I, II, and III: 0.

12) Compatibility with other oils per FTM 791 Method 3403: All viscosity grades shall pass.

40 13) Elastomer Compatibility, % swelling, acceptable range for all viscosity grades after 72 hours per FTM 791 Method 3604 (except conducted with the specific materials and temperatures herein listed):

| <u>Material</u> | <u>Test Temperature</u> | <u>Acceptable Limits</u> |
|-------------------------|-------------------------|--------------------------|
| AMS-3217/1 | 70°C (158°F) | - 5 to + 5 |
| AMS-3217/4 | 150°C (302°F) | - 5 to + 5 |
| AMS-3217/5 | 150°C (302°F) | - 5 to + 5 |
| US Navy Silicone Rubber | 121°C (250°F) | 0 to + 20 |

50 14) Trace Metal Content, ppm, maximum for all viscosity grades, per test method of Paragraph 4.5.2 of MIL-L-22851D (1 December 1990) or equivalent: Iron, 5; Silver, 3; Aluminum, 7; Chromium, 5; Copper, 3; Magnesium, 3; Nickel, 3; Lead, 5; Silicon, 25; Tin, 10; Titanium, 2; Molybdenum, 4.

55 10. Apparatus which comprises in combination (i) at least one four stroke cycle, reciprocating piston aircraft engine, (ii) at least one fuel storage tank operatively connected with said at least one engine so as to deliver fuel required to operate said engine, and (iii) at least one chamber in said engine for receiving and maintaining a supply of lubricating oil for lubricating said engine during operation thereof, wherein said

5 at least one fuel storage tank contains an unleaded aviation gasoline composition which comprises a blend of hydrocarbons and at least one cyclopentadienyl manganese tricarbonyl compound dissolved therein in an amount such that said gasoline composition has a minimum knock value lean rating octane number of 100 as determined by ASTM Test Method D2700 and wherein Motor Method octane ratings are converted to aviation ratings in the manner described in ASTM Specification D910-90, said composition being further characterized by having:

- 10 a) a distillation temperature as determined by ASTM Test Method D86 of 10% evaporated, 167°F maximum temperature; 40% evaporated, 167°F maximum temperature; 90% evaporated, 275°F maximum temperature; and a final boiling point of 338°F maximum temperature; the sum of the 10 and 50% evaporated temperatures being 307°F minimum; the distillation recovery being 97% minimum; the distillation residue being 1.5% maximum; and the distillation loss being 1.5% maximum;
 - 15 b) a heat of combustion as determined by ASTM Test Method D1405 and as calculated from Table 1 thereof of 18,720 btu per pound minimum, or a heat of combustion as determined by ASTM Test Method D2382 of 18,700 btu per pound minimum, the latter method controlling in case of a discrepancy there-between;
 - 20 c) a vapor pressure as determined by ASTM Test Method D323 or D2551 of 5.5 psi minimum and 7.0 psi maximum;
 - d) a copper strip corrosion as determined by ASTM Test Method D130 of number 1, maximum;
 - e) a potential gum (5-hour aging gum) as determined by ASTM Test Method D873 of 6 mg per 100 mL maximum, or a potential gum (16-hour aging gum as determined by ASTM Test Method D873) of 10 mg per 100 mL;
 - f) a sulfur content as determined by ASTM Test Method D1266 or D2622 of 0.05 % by weight maximum;
 - 25 g) a freezing point as determined by ASTM Test Method D2386 of -72°F maximum; and
 - h) a water reaction as determined by ASTM Test Method D1094 wherein the volume change, if any, does not exceed \pm 2 mL;
- and wherein said at least one chamber contains as the lubricating oil for said engine a lubricating oil composition satisfying the chemical and physical property requirements set forth below:

1) Viscosity, cSt, per ASTM D 445:

| | <u>SAE Grade</u> | <u>Minimum at 100°C</u> | <u>Less than at 100°C</u> |
|----|------------------|-------------------------|---------------------------|
| | 30 | 9.3 | 12.5 |
| | 40 | 12.5 | 16.3 |
| | 50 | 16.3 | 21.9 |
| 35 | 60 | 21.9 | 26.1 |

- 2) Multigrade oil shall meet the viscosity requirements and the Low Temperature Viscosity Cold Crank Simulation requirements of SAE Test Method J300 for the designated grade.
- 40 3) Viscosity Index, minimum per ASTM D 2270: 100 for SAE grades 30, 40 and Multigrade; 95 for SAE grades 50 and 60.
- 4) Flash Point, °C, minimum per ASTM D 92: 220 for SAE grades 30 and Multigrade; 225 for SAE grade 40; and 243 for SAE grades 50 and 60.
- 5) Pour Point, °C, maximum per ASTM D 97: -24 for SAE grade 30; -22 for SAE grade 40; and -18 for SAE grades 50 and 60.
- 45 6) Viscosity, High Temperature, High Shear at 150 °C, cP, minimum per ASTM D 4683, D 4741, D 4624: 3.3 for all viscosity grades.
- 7) Total Acid Number, mg KOH/g, maximum (titrated to a pH 11 end point) per ASTM D 664: 1.0 for all viscosity grades.
- Ash Content, Mass %, maximum per ASTM D 482: 0.006 for all viscosity grades.
- 50 9) Trace Sediment, mL/100 mL Oil, maximum per ASTM D 2273: 0.005 for all viscosity grades.
- 10) Copper Strip Corrosion, maximum rating per ASTM D 130: 1 after 3 hours @ 100°C for all viscosity grades; and 3 after 3 hours @ 204°C for all viscosity grades.
- 11) Foaming Tendency/Stability per ASTM D 892: Aerated Volume, mL, maximum for all viscosity grades per Sequences I, II and III: 50; Volume after 10 minutes, mL, maximum for all viscosity grades per Sequences I, II, and III: 0.
- 55 12) Compatibility with other oils per FTM 791 Method 3403: All viscosity grades shall pass.
- 13) Elastomer Compatibility, % swelling acceptable range for all viscosity grades after 72 hours per FTM 791 Method 3604 (except conducted with the specific materials and temperatures herein list-

ed):

| <u>Material</u> | <u>Test Temperature</u> | <u>Acceptable Limits</u> |
|-------------------------|-------------------------|--------------------------|
| AMS-3217/1 | 70°C (158°F) | - 5 to + 5 |
| AMS-3217/4 | 150°C (302°F) | - 5 to + 5 |
| AMS-3217/5 | 150°C (302°F) | - 5 to + 5 |
| US Navy Silicone Rubber | 121°C (250°F) | 0 to + 20 |

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14) Trace Metal Content, ppm, maximum for all viscosity grades, per test method of Paragraph 4.5.2 of MIL-L-22851D (1 December 1990) or equivalent: Iron, 5; Silver, 3; Aluminum, 7; Chromium, 5; Copper, 3; Magnesium, 3; Nickel, 3; Lead, 5; Silicon, 25; Tin, 10; Titanium, 2; Molybdenum, 4.

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European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 30 9836

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | CLASSIFICATION OF THE APPLICATION (Int. CL.5) | | | | | | |
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| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | | | | | | | |
| P,A | EP-A-0 466 511 (ETHYL PETROLEUM ADDITIVES) * claims 1,2,3,7,8 * * table PAGE6 * | 1,3 | C10L1/30 | | | | | | |
| A | GB-A-2 186 287 (INSTITUT FRANCAIS DU PETROLE) * claim 1 * * examples 1,2 * | 1 | | | | | | | |
| A | KIRK-OTHMER 'ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY EDITION 3, VOLUME 3' , JOHN WILEY AND SONS , NEW YORK * page 332 * | 1 | | | | | | | |
| A | NELSON 'PETROLEUM REFINERY ENGINEERING EDITION 4' , MC GRAW HILL , NEW YORK * page 34; tables 3-6 * | 1 | | | | | | | |
| | | | TECHNICAL FIELDS SEARCHED (Int. CL.5) | | | | | | |
| | | | C10L | | | | | | |
| <p>The present search report has been drawn up for all claims</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%;">Place of search</td> <td style="width: 33%;">Date of completion of the search</td> <td style="width: 34%;">Examiner</td> </tr> <tr> <td>THE HAGUE</td> <td>02 FEBRUARY 1993</td> <td>OSWALD DE HERDT</td> </tr> </table> | | | | Place of search | Date of completion of the search | Examiner | THE HAGUE | 02 FEBRUARY 1993 | OSWALD DE HERDT |
| Place of search | Date of completion of the search | Examiner | | | | | | | |
| THE HAGUE | 02 FEBRUARY 1993 | OSWALD DE HERDT | | | | | | | |
| <p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document</p> | | | | | | | | | |